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Spectrophotometric Determination of Nickel after Separation by Adsorption of its DDTC Chelate on Microcrystalline Naphthalene

Masatada SATAKE*

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A method is presented for the determination of trace amounts of nickel after separation by adsorption of nickel DDTC chelate on microcrystalline naphthalene. Nickel reacts with DDTC to form a stable chelate, which is quantitatively adsorbed on microcrystalline naphthalene at room temperature. The mixture of the chelate and naphthalene is separated from aqueous solution and dissolved in dimethylformamide. The absorbance of the solution is measured at 382 nm against the reagent blank. Other factors such as pH, amounts of DDTC and naphthalene, digestion, shaking time, standing time and diverse ions are studied. The Beer's was obeyed over the range of 5-100 μg nickel in 10 ml of dimethylformamide solution. The molar absorptivity was 5.9×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$ at 382 nm, the sensitivity being 0.010 μg nickel per cm^2 for an absorbance of 0.001. The precision of this method was estimated with ten sample solutions containing 60 μg of nickel. A mean absorbance at 382 nm was 0.600 with a relative standard deviation of 0.64%.

1 Introduction

Sodium diethyldithiocarbamate(abbreviated as DDTC) forms water-insoluble metal chelates with various metals such as copper, iron(II), iron(III), cobalt, bismuth, nickel, uranium(IV), chromium(IV), zinc, lead, cadmium. These chelates are easily extracted into chloroform or methl isobutyl ketone and trace amounts of metals are determined by spectrophotometry or atomic absorption spectrophotometry.

We have found that metal chelates are quantitatively extracted into molten naphthalene at the elevated temperature. However, the method is more complicate in the experimental operation than a simple chloroform extraction method.

We have developed a new method of analysis involving adsorption

* Division of Applied Science

adsorption of metal chelates on microcrystalline naphthalene and their subsequent spectrophotometric determinations, and demonstrated for palladium [1] and nickel [2] with α-furildioxime and copper [3] with Ammonium Pyrrolidine dithiocarbamate. The present communication describes the optimum conditions for an improved procedure for the adsorption of nickel-DDTC chelate on micrcrystalline naphthalene at room temperature(~25°) and subsequent determination of this metal spectrophotometrically after dissolution of the naphthalene mixture in dimethylformamide.

2 Experimental method

2.1 Reagents

Standard nickel solution, 10 ppm. Prepared by diluting 10 ml of standard nickel solution(1000 ppm, Wako Pure Chemical Industries,Osaka, Japan) to 1000 ml with deionized water.

DDTC solution, 0.2%. Prepared by dissolving 0.2 g of DDTC in 100 ml of deionized water.

Naphthalene solution, 20%. Prepared by dissolving 20 g of naphthalene in acetone and diluting to 100 ml.

Buffer solutions. Prepared by mixing 1M acetic acid and 1M ammomium acetate solution for pH 3-6; 1M aqueous ammonia and 1M ammonium acetate solution for pH 8-11.

Naphthalene, acetone and all other reagents were of analytical reagent grade, and were used without further purification.

2.2 Apparatus

A Hitachi Model 200-20 double beam spectrophotometer was used for the absorbance measurements.

All pH measurements were done with a Toa-Dempa, HM-5A, pH meter, equipped with a combination calomel and glass electrode assembly.

Naphthalene was dried with a Tabai Model K-2 dryer(Tabai Mfg.Ltd., Japan).

2.3 Procedure

Transfer about 40 ml of sample solution containing 60 μg of nickel to a tightly stoppered Erlenmeyer flask, adjust to about pH 5.5 with the acetate buffer solution and add 2.0 ml of 0.2% DDTC solution. Mix the solution well and stand for 10 min. Transfer into this solution as fast as possible 2.0 ml of 20% naphthalene solution using a small nozzled pipet attached to a rubber bulb, and shake vigorously for 1 min. Separate the solid by filtration using a filter paper (e.g., No5C, Toyo Roshi Co. Japan) placed flat on a filter plate in a funnel, or through a sintered glass filter(No2). Wash with water and dry at 50-60°C in a dryer. Then dissolve the product in dimethyl-

formamide and make up to 10 ml. Measure the absorbance of the solution in a 10-mm glass cell at 382 nm against a reagent blank prepared similarly.

3 Results and discussion

3.1 Absorption spectra

Sample solution containing 60 μg of nickel, 2.0 ml of the buffer solution and 2.0 ml of 0.2% DDTC solution was prepared according to the procedure and the adsorption of the chelate was carried out. Figure 1 shows the absorption spectra of reagent blank and nickel chelate in naphthalene-dimethylformamide solution, measured against water in 360 to 460 nm range. The absorption curve of the chelate has two peaks at 382 and 392 nm, whereas the absorption of the reagent blank is almost negligible above 380 nm. Therefore, 382 nm was adopted as the optimum wavelength throughout this work.

3.2 Effect of pH

The effect of pH on the absorbance of the chelate was investigated with the sample containing 60 μg of nickel, 2.0 ml of 0.2% DDTC solution and 2.0 ml of the buffer solution. The pH measurements was made after adsorption of the chelate. The absorbance variation against pH, is shown in Fig.2. The absorbance of the chelate depend on pH, and maximum absorbance is obtained between 3.0 and 8.5. It decreases slightly above pH 8.5. Consequently, a pH of 5.5 was chosen as the optimum condition for this work.

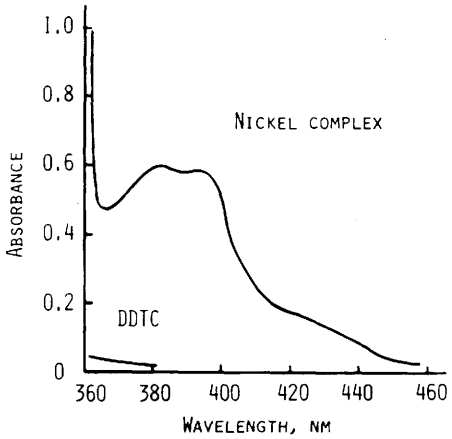

FIG. 1 ABSORPTION SPECTRA OF DDTC AND NICKEL COMPLEX IN NAPHTHALENE-DMF SOLUTION
NI : 60 μG ; PH : 5.5 ; 0.2%DDTC : 2.0 ML ; DIGESTION TIME : 5 MIN ; 20% NAPHTHALENE : 2 ML ; REFERENCE : WATER ; (1) DDTC, (2) NICKEL COMPLEX

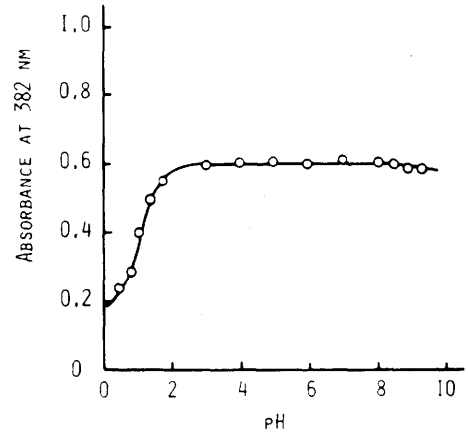

FIG. 2 EFFECT OF PH
NI : 60 μG ; 0.2% DDTC : 2.0 ML ; DIGESTION TIME : 5 MIN ; 20% NAPHTHALENE : 2 ML ; SHAKING TIME : 2 MIN ; STANDING TIME : 15 MIN
REFERENCE : REAGENT BLANK

3.3 Effect of reagent concentration

Varying amounts of DDTC reagent were added to the samples containing 60 μg of nickel and 2.0 ml of the buffer solution, and variations in the absorbance of the chelate were studied at 382 nm. The results are shown in Fig.3. It can be seen that the adsorption of the chelate increased with increasing amounts of added DDTC solution up to 0.4 ml of 0.2% DDTC solution and then remained almost constant between 0.4 and 5.0 ml. Consequently, 2.0 ml of 0.2% DDTC solution were found sufficient for the absorbance measurements.

3.4 Effect of addition of buffer solution

The various amounts of the acetate buffer solution(pH 5.5) were added to the sample solutions containing 60 μg of nickel and 2.0 ml of 0.2% DDTC solution, and the adsorption was performed according to the procedure. Figure 4 shows the effect of the buffer solution on the absorbance. It was found from the Figure that the adsorption of the chelate did not given the effect on the absorbance over the range of 0.5-5.0 ml of the buffer solution. Therefore, 2.0 ml of the buffer solution were used for the absorbance measurements.

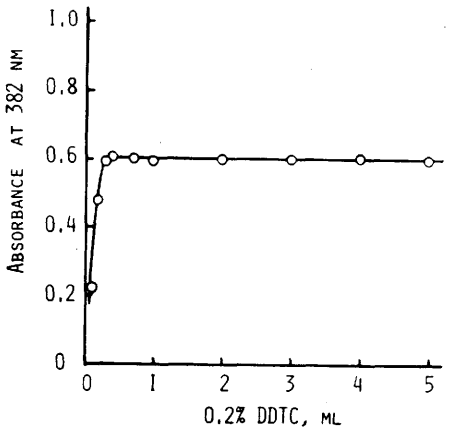

FIG. 3 EFFECT OF REAGENT CONCENTRATION
NI: 60 μG ; PH : 5.5 ; DIGESTION TIME : 5 MIN ; 20% NAPHTHALENE : 2 ML ; SHAKING TIME : 2 MIN ; REFERENCE : REAGENT BLANK

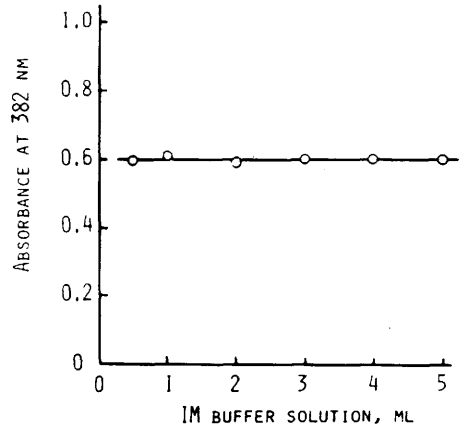

FIG. 4 EFFECT OF BUFFER SOLUTION
NI : 60 μG ; PH : 5.5 ; 0.2% DDTC : 2.0 ML DIGESTION TIME : 5 MIN ; 20% NAPHTHALENE : 2.0 ML ; SHAKING TIME : 2 MIN
REFERENCE : REAGENT BLANK

3.5 Effect of digestion time

The nickel chelate in the solution containing 60 μg of nickel and 2.0 ml of 0.2% DDTC solution at pH 5.5 was digested at room temperature, and the effect of digestion time on the absorbance was investigated between 5 and 50 min. The results are shown in Fig.5.

The absorbance is constant independently of digestion time. Therefore, a 5 min of digestion time was selected foe the further work.

3.6 Effect of naphthalene concentration

The various amounts of naphthalene were added to the sample solution containing the nickel chelate, and the adsorption of the chelate was performed according to the procedure. Figure 6 shows the effect of addition of naphthalene on the absorbance. From the experimental data, the addition of 0.2 - 4.0 ml of 20% naphthalene solution did not cause the effect on the absorbance. Therefore, 2.0 ml of 20% naphthalene solution were used for the further work.

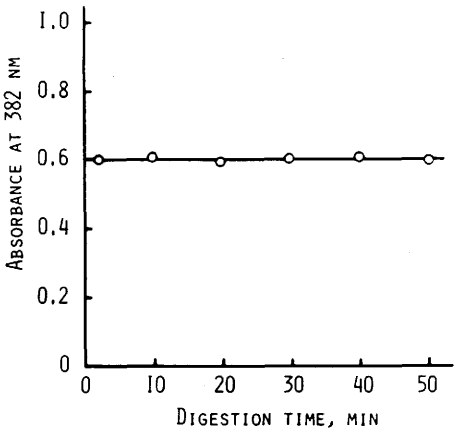

FIG. 5 EFFECT OF DIGESTION TIME
Ni : 60 μG ; pH : 5.5 ; 0.2% DDTC : 2.0 ML ;
20% NAPHTHALENE : 2 ML ; SHAKING TIME : 2 MIN ;
REFERENCE : REAGENT BLANK

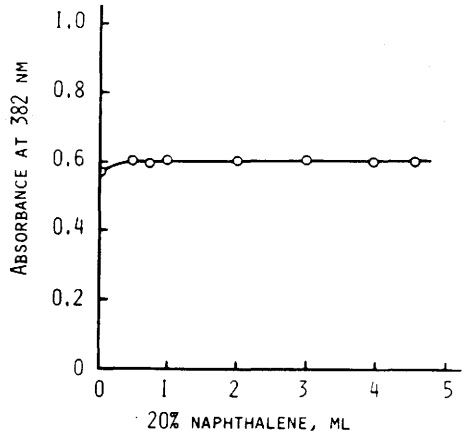

FIG. 6 EFFECT OF NAPHTHALENE CONCENTRATION
Ni : 60 μG ; pH : 5.5 ; 0.2% DDTC : 2.0 ML ;
DIGESTION TIME : 5 MIN ; SHAKING TIME : 2 MIN
REFERENCE : REAGENT BLANK

3.7 Effect of shaking time

The effect of shaking time on the adsorption of the nickel chelate was examined. The results are shown in Fig.7. The adsorption of the nickel chelate was completed after several seconds. Therefore, 1 min of shaking time was selected for the further work.

3.8 Effect of aqueous volume

The volume of aqueous phase containing fixed nickel and DDTC reagent was varied from 50 to 300 ml, and the adsorptive operation were carried out by the procedure. The results are shown in Fig.8. The adsorption was almost constant over the range 50-120 ml, and then decreased gradually with the volume in aqueous phase.

3.9 Effect of standing time

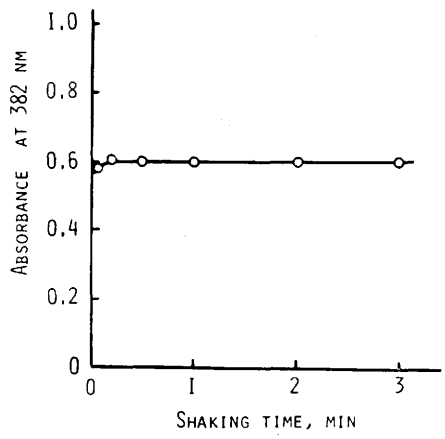

FIG. 7 EFFECT OF SHAKING TIME
Ni : 60 μG ; pH : 5.5 ; 0.2% DDTC : 2.0 ML ;
20% NAPHTHALENE : 2 ML ; STANDING TIME : 15 MIN
REFERENCE : REAGENT BLANK

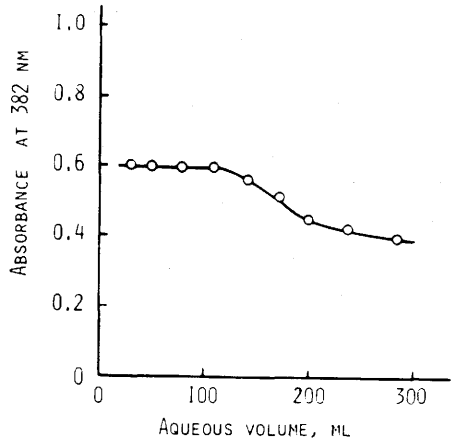

FIG. 8 EFFECT OF AQUEOUS VOLUME
Ni : 60 μG ; pH : 5.5 ; 0.2% DDTC : 2.0 ML ;
DIGESTION TIME : 5 MIN ; 20% NAPHTHALENE : 2 ML ;
SHAKING TIME : 5 MIN ; STANDING TIME : 15 MIN
REFERENCE : REAGENT BLANK

The mixture of the nickel chelate and naphthalene was dissolved in dimethylformamide, and the effect of standing time on the absorbance was examined. From the experimental result, the color of the nickel chelate was stable for a long time. Therefore, 15 min of standing time were selected for the further work.

3.10 Calibration curve

Under the optimum conditions described above, a calibration curve for nickel chelate in dimethylformamide was constructed at 382 nm. It was found to be linear over the concentration range of 5-100 μg nickel in 10 ml of dimethylformamide. The results are shown in Fig.9. The molar absorptivity of the chelate was found to be 5.9×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$, while the sensitivity was 0.010 $\mu g \cdot cm^{-2}$ for nickel for 0.001 absorbance. Ten replicate analysis of samples containing 60 μg of nickel gave a mean absorbance of 0.600 with relative standard deviation of 0.64%.

3.11 Choice of solvent

Various solvents were tested to dissolve the adsorbed nickel-DDTC chelate along with microcrystalline naphthalene. The chelate mixture is soluble in acetonitrile, benzene, toluene, xylene, chlorobenzene, o-dichlorobenzene, dichloroethane, chloroform, acetone, MIBK, isoamyl-acetate and propylene carbonate. It is decolorized in dioxane after several min.

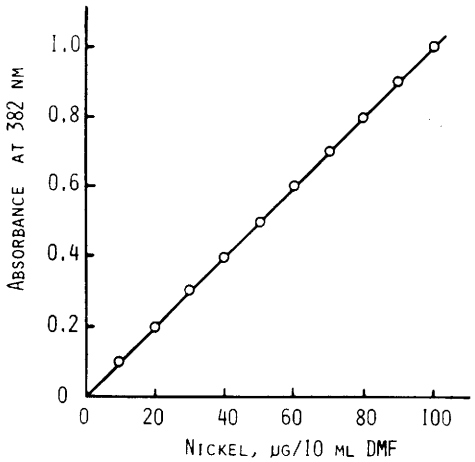

FIG. 9 CALIBRATION CURVE FOR NICKEL
pH : 5.5 ; 0.2% DDTC : 2.0 ML ; DIGESTION TIME : 5 MIN ; 20% NAPHTHALENE : 2 ML ; SHAKING TIME : 2 MIN ; STANDING TIME : 15 MIN
REFERENCE : REAGENT BLANK

3.12 Effect of diverse ions

Alkali metal salts and metal ions were added to the solutions containing 60 μg of nickel and the described procedure was applied. The analytical data are shown in Table I and II. The following species did not interfered : Na_2SO_4, NaCl, NH_4Cl, NaH_2PO_4, Na_2HPO_4, Na_2CO_3, KBr, Na_2SO_4, CH_3COONa, Ca(II), Zn(II), Mn(II), Pt(II), Pb(II), Mg(II), Al(III). Na_2SO_4, Cr(IV), Fe(III), Hg(II), Co(II), Bi(III) and Cu(II) gave positive interference, and KCN and Cd(II) did negative one. Especially EDTA, KCN, Fe(III), Co(II), Bi(III) and Cu(II) interfered seriously.

Table I Effect of diverse alkali salts

Diverse alkali salts	Amount added(mg)	Absorbance(382 nm)
———	——	600
Na_2SO_4	700	606
NaCl	700	601
NH_4Cl	700	601
$NaH_2PO_4 \cdot 2H_2O$	700	610
$Na_2HPO_4 \cdot 12H_2O$	700	610
Na_2CO_3	700	600
Na_2SO_3	300	610
"	500	630

"	700	0.658
Na_2SO_4	700	0.599
CH_3COONa	700	0.608
KBr	1000	0.607
KCN	0.01	0.603
"	0.05	0.606
"	0.10	0.608
"	1.00	0.000
EDTA	0.01	0.600
"	0.05	0.559
"	0.10	0.469
"	1.00	0.000
Sodium tartrate	300	0.610
"	500	0.630
Sodium citrate	700	0.602

Ni : 60 μg ; pH : 5.5 ; 0.2% DDTC : 2.0 ml

Table II Effect of diverse metal ions

Diverse metal ions	Amount added(μg)	Absorbance(382 nm)
———	———	0.600
Ca(II)	1000	0.610
Zn(II)	500	0.603
Cr(VI)	10	0.613
"	100	0.678
"	500	0.732
Mn(II)	1000	0.600
Cd(II)	500	0.618
"	1000	0.393
Fe(III)	1	0.611
"	5	0.650
"	50	1.421
Hg(II)	50	0.611
"	100	0.627
Pt(IV)	500	0.610
"	1000	0.624
Pb(II)	100	0.618
Mg(II)	100	0.605

Co(II)	5	0.696
"	10	0.791
"	50	1.486
Al(III)	500	0.604
Bi(III)	5	0.622
"	10	0.644
"	100	0.973
Cu(II)	10	0.629
"	50	0.721
"	100	0.857

Ni(II) : 60 μg ; pH : 5.5 ; 0.2% DDTC : 2.0 ml